

# PATENT SPECIFICATION

1,165,637

NO DRAWINGS.

Inventors:—KENNETH RICHARD PAYNE and  
MALCOLM HOWARD MILNES.

Date of filing Complete Specification: 19 July, 1968.

Date of Application (No. 33127/67): 19 July, 1967.

Complete Specification Published: 1 Oct., 1969.

1,165,637



Index at acceptance:—C2 C(KB22Y, KB220, KB227, KB30Y, KB332, KB34Y, KB340, KB627, KB71Y, MK22Y, MK220, MK227, MK29Y, MK292, MK30Y, MK31Y, MK313, MK314, MK332, MK338, MK36Y, MK365, MK470, MK475, MK476, MK621, MK631, MK661, MK662).

International Classification:—C 07 c 79/24.

## COMPLETE SPECIFICATION.

### Production of Nitrophenols.

We, COALITE AND CHEMICAL PRODUCTS LIMITED, a British Company, of Butter-milk Lane, Bolsover, near Chesterfield, Derbyshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of nitrophenols, particularly but not exclusively 4-nitrophenols, and includes a process for the purification of the nitrophenols.

It is known to produce 4-nitrophenols by the nitrosation with nitrous acid of a phenol having no substituent in the 4-position, followed by oxidation of the nitroso compound with nitric acid. The process is carried out in two distinct stages with isolation of the nitroso compound produced in the first stage. Close control of the temperature in the two stages is necessary, the first or nitrosation stage being carried out at a temperature from  $-10^{\circ}\text{C}$  to  $+5^{\circ}\text{C}$  and the second or oxidation stage being carried out at a temperature in the range  $0-40^{\circ}\text{C}$ , preferably about  $20^{\circ}\text{C}$ .

It has now been found that the process can advantageously be carried out without intermediate isolation of the nitroso compound.

According to the invention, a process for the production of a nitrophenol comprises nitrosating a phenol which is un-

substituted in at least one position and, without separating the nitroso compound, oxidising the nitroso group or groups to a nitro group or nitro groups.

According to the invention furthermore, there is provided a process for the production of a 4-nitrophenol which comprises nitrosating a phenol which is unsubstituted in the 4-position and, without isolating the 4-nitrosophenol so produced, oxidising the nitroso compound to the nitro compound.

The process is suitably carried out in a single reaction vessel or zone and thus virtually constitutes a process of directly converting the phenol into a nitro derivative.

The nitrosation may be carried out at a temperature of from  $-40^{\circ}\text{C}$  to  $+5^{\circ}\text{C}$ . In the oxidation stage, the reaction mixture suitably contains 5–25%, preferably about 15%, by weight of nitric acid.

The process is particularly suitable for converting *m*-cresol into its 4-nitro derivative but other alkylphenols and other substituted phenols, for example, chlorophenols or bromophenols, may be used as reactants provided that the 4-position is unsubstituted. Phenol itself may also be converted into its 4-nitro derivative.

Purification of the crude nitrophenol, for example 4-nitro-*m*-cresol, is preferably effected by converting the nitrophenol into an alkali metal salt thereof, suitably the sodium salt, separating the salt and regenerating the nitrophenol from the salt by acidification. The separation of the salt

may comprise the steps of crystallisation and/or filtration or the salt may be separated from the mother liquor by centrifuging the centrifuged salt being then preferably washed with water.

Such method of purification is far more satisfactory than that of dissolving the crude nitrophenol itself in a solvent followed by crystallisation of the nitrophenol from the solution, in that it is simpler, very effective and merely entails care in the control conditions which may require variation according to the nature of the impurities and/or the particular nitrophenol. However, any such variation which may be required in the conditions may readily be found by simple trial-and-error experiment.

The invention further provides 4-nitro-2,3-xyleneol as a new compound. The compound may, inter alia, be used as an intermediate for the production of, for example, the corresponding 4-amino compound by reduction of the nitro compound.

The invention is illustrated in the following examples.

#### EXAMPLE 1

108g (1 mole) of *m*-cresol were added to a solution composed of 200 ccs of water, 24 g (0.6 mole) caustic soda and 82.8g (1.2 moles) sodium nitrite, the whole forming a homogeneous mixture at room temperature. This mixture was added slowly but with rapid agitation to a solution consisting of 105 ccs of water and 210 ccs of concentrated hydrochloric acid maintained at a temperature not exceeding 5°C. After all the *m*-cresolate had been added, stirring for a further 30 minutes ensured completion of the nitrosation. (In a concurrent run, the 4-nitroso-*m*-cresol, M.P. 155°C d., was isolated at this stage of the reaction and the yield was found to be 91% molar). The reaction mixture was allowed to warm up to room temperature, all excess oxides of nitrogen being thereby expelled. 133 ccs (189 g) of concentrated nitric acid were added to the stirred reaction mixture at room temperature. 134 g (0.875 mole) of 4-nitro-*m*-cresol (M.P. 122°C) were isolated from the reaction product, a molar yield of 96% based in the nitroso compound. The total molar yield based on *m*-cresol was 87.5%.

The run was repeated with the use of sulphuric acid in place of hydrochloric acid in the nitrosation stage. Similar results were obtained.

#### EXAMPLE 2

128.5 g (1 mole) of 2-chlorophenol was added to a solution of 1200 ccs water, 56 g (1.4 moles) caustic soda and 103.5 g (1.5 moles) sodium nitrite. The mixture was

slowly added to a well agitated mixture of 154 ccs of concentrated sulphuric acid and 2400 ccs of water held at -5°C. After half an hour's stirring when all the chlorophenolate had been added, the mixture was allowed to warm up to room temperature and 635 ccs (900 g) of concentrated nitric acid were added. On completion of the oxidation, 87.2 g (0.504 mole) of 2-chloro-4-nitro phenol, M.P. 109°C, were obtained, a 50.4% molar yield based on the 2-chlorophenol.

#### EXAMPLE 3

122g (1 mole) of 2,3-xyleneol were added to a solution of 250 ccs water, 40 g (1 mole) caustic soda and 82.8 g (1.2 mole) sodium nitrite. This mixture was slowly added to a mixture to 350 ccs of water and 250 ccs of concentrated hydrochloric acid with vigorous agitation at 0°-5°C. After the addition and an extra half hour's reaction time, the whole mixture was treated with 300 mls (425 g) concentrated nitric acid and the oxidation allowed to proceed at 20°C. On filtration, 142 g of crude nitro-xyleneol was obtained and this was subjected to steam distillation. Prolonged steam distillation was required to remove the more volatile 4,6-dinitro-2,3-xyleneol. Extraction of the steam distillate with ether yielded 92 g of the 4,6-dinitro-2,3-xyleneol, M.P. 85°C.

The residue from the steam distillation was leached several times with boiling water and the extracts were crystallised. This gave 48 g of impure 4-nitro-2,3-xyleneol, M.P. 117°C. This was purified through its sodium salt in a manner similar to that hereinafter described in Example 5. Pure 4-nitro-2,3-xyleneol was thereby obtained in the form of pale yellow needles, M.P. 126°C. Its phenylurethane derivative had a M.P. of 145°C. The molar yield of the 4-nitro-2,3-xyleneol was 35.0% and that of the 4,6-dinitro-2,3-xyleneol was 43.4%.

#### EXAMPLE 4

100 g (0.655 mole) of the technical or crude 4-nitro-*m*-cresol, M.P. 122°C, obtained in Example 1, was stirred into a mixture of 200 ccs water and 43.5 g (1.09 mole) caustic soda. The whole mixture was warmed to 60°C with stirring, then cooled and filtered.

The filtrate was suspended in 500 ccs water, stirred vigorously and acidified with dilute hydrochloric acid. The product after filtering and drying was 95.7 g (0.625 mole) 4-nitro *m*-cresol, M.P. 128°C, of 100% purity, representing 95.7% recovery.

#### EXAMPLE 5

157 g (1 mole) technical 4-nitro-2,5-xyleneol, melting point 112°C, as obtained

by nitrosation-oxidation of 2,5-xyleneol in accordance with the process of the invention, were stirred into a mixture of 67 g (1.67 moles) caustic soda and 304 ccs water. The whole mixture was warmed to 60°C and cooled with stirring to 15°C. The sodium 4-nitro-2,5-xyleneate was then centrifuged rigorously free from the alkyl-ine mother liquors, suspended in 750 ccs water, stirred, and acidified with dilute hydrochloric acid. The filtered, dried product was 133.5 g (0.85 mole) of substantially pure 4-nitro-2,5-xyleneol, melting point 121°C. This represented 85.0% recovery.

#### EXAMPLE 6

173.5 g (1 mole) crude 4-nitro-2-chlorophenol, melting point 103°C, were stirred into a mixture of 67 g (1.67 mole) caustic soda and 332 ccs water, warmed to 60°C, stirred and the sodium salt crystallised. After working up in the usual way the sodium 4-nitro-2-chlorophenolate was suspended in 1 litre of water and slowly acidified with dilute hydrochloric acid. Upon filtration and drying, the product 4-nitro-2-chlorophenol (157.0 g 0.905 mole) had a melting point of 110°C and was substantially pure. This represented 90.5% recovery.

#### EXAMPLE 7

A stirred 75-gallon vessel containing 15 gallons of water was charged with 20 lbs of 2-chlorophenol, 16 lbs caustic soda and 9 lbs sodium nitrite and the whole mixture was maintained at 5°C. The mixture was pumped slowly into a similar vessel containing 40 gallons of water and 26 lbs of concentrated sulphuric acid at -5°C. When all the chlorophenolate had been pumped in, the temperature was increased to 20°C and 10 gallons of 70% nitric acid were added. Upon completion of the oxidation, the product was centrifuged, washed and dried, 21.5 lbs of 2-chloro-4-nitrophenol, M.P. 109°C, being obtained, a molar yield of 79.5% based on the 2-chlorophenol.

3-Chlorophenol has been subjected to nitrosation/oxidation in a similar manner, the nitro product being substantially completely the 4-nitro derivative.

#### EXAMPLE 8

A mixture of 0.5 mole 2,5-dichlorophenol, 0.75 mole sodium nitrite, 0.5 mole caustic soda and 1 litre water was slowly added to 1100 ccs of 10% hydrochloric acid at 0-5°C. This gave a 54% mole yield of 4-nitroso-2,5-dichlorophenol. Oxidation was then achieved by the addition of 400 ccs. conc. nitric acid and warming to 20°C. The mixture was worked up by steam distillation and crystallisation from

boiling water, 4-nitro-2,5-dichlorophenol (M.P. 117°C) and the 2,4-dinitro-3,6-dichlorophenol (M.P. 146°C) being thereby isolated.

2,6-, 2,3- and 3,5-dichlorophenols have also been subjected to the nitrosation/oxidation process according to the invention with the production of the corresponding dichloro-4-nitrophenols. The dichlorophenols are less readily nitrosated than the monochlorophenols and the alkylphenols.

#### WHAT WE CLAIM IS:—

1. A process for the production of a nitrophenol, which comprises nitrosating a phenol which is unsubstituted in at least one position and, without separating the nitroso compound, oxidising the nitroso group or groups to a nitro group or nitro groups.

2. A process for the production of a 4-nitrophenol, which comprises subjecting to nitrosation a phenol which is unsubstituted in the 4-position to the phenolic hydroxyl group and, without separating the nitroso compound, oxidising the nitroso group to the nitro group.

3. A process according to claim 1 or claim 2, in which the nitrosation and oxidation are carried out in the same vessel or zone.

4. A process according to any one of the preceding claims, in which the oxidation is effected with nitric acid.

5. A process according to claim 4, in which the nitric acid forms 5-25% by weight of the reaction mixture.

6. A process according to any one of the preceding claims, in which the phenol is an alkyl-phenol.

7. A process according to claim 6, in which the phenol is *m*-cresol.

8. A process according to claim 6, in which the phenol is a xyleneol.

9. A process according to claim 8, in which the xyleneol is the 2,3-isomer.

10. A process according to claim 8, in which the xyleneol is the 2,5-isomer.

11. A process according to any one of claims 1 to 5, in which the phenol is a chloro- or bromo-phenol.

12. A process according to any one of claims 1 to 5, in which the phenol is 2-chlorophenol.

13. A process according to any one of claims 1 to 5, in which the phenol is 3-chlorophenol.

14. A process according to any one of claims 1 to 5, in which the phenol is a dichlorophenol.

15. A process according to any one of claims 2 to 14, in which the 4-nitrophenol is separated in the form of an alkali metal salt and the salt is acidified to release the nitrophenol.

16. A process according to any one of claims 1 to 14, including the steps of separating crude nitrophenol from the reaction mixture, converting the nitrophenol or nitrophenols into an alkali metal salt thereof, separating the alkali metal salt from mother liquor and regenerating the nitrophenol from the said by acidification.
17. A process according to claim 15 or claim 16, in which the alkali metal salt is the sodium salt.
18. A process according to claim 16, in which the salt is separated from the mother liquor by centrifuging.
19. A process according to claim 18, in which the centrifuged salt is washed with water.
20. A process according to any one of claims 15 to 19, in which the nitrophenol is converted to an alkali metal salt by reaction with aqueous sodium hydroxide.
21. A process for the production of a 4-nitrophenol, substantially as hereinbefore described with reference to any one of Examples 1, 2, 3, and 7.
22. A process for the purification of a crude 4-nitrophenol obtained by the process claimed in claim 1, substantially as hereinbefore described with reference to any one of Examples 3, 4, 5, and 6.
23. A nitrophenol whenever obtained by the process claimed in any one of the preceding claims.
24. 4-nitro-2,3-xyleneol.
- EDWARD EVANS & CO.,  
53—64 Chancery Lane,  
London, W.C.2.  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1969.  
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,  
from which copies may be obtained.